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## COMPLETE SPECIFICATION

### NO DRAWINGS

### Method of Treating Glass Articles

I, FREDRIK WILHELM ANTON KURZ, a Swedish subject of Nysätravägen 12, Lidingö, Sweden, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of treating glass articles to improve the chemical resistance of the glass. More particularly, the invention relates to a method of treatment of alkali-lime-silicate glass for this purpose.

Common alkali-lime-silicate glass shows under certain circumstances an insufficient chemical resistance and thus also a reduced mechanical resistance; it is not completely resistant to water vapour, therefore it will also eventually be weakened mechanically. This is explained by the fact that close to the surface of the glass, the alkali content may be leached out by condensed moisture from the air. These disadvantages of the alkali-lime-silicate glass may be avoided by using instead, e.g. borosilicate glass, neutral glass or silica glass, but these glasses have the disadvantage that they are considerably more expensive to manufacture.

The present invention has for an object to treat alkali-lime-silicate glass so as to improve its chemical resistance, by modifying the composition of the said glass by incorporating components which improve the chemical resistance of the glass near the surface, so that a surface layer having an enhanced chemical and mechanical resistance results. Preferably, this treatment is combined with a treatment which results in elimination of alkali from the surface layer of the glass. Such a removal of alkali from the surface layer tends to improve the resistance of the glass, since moisture attacks mainly the surface. A decrease of the alkali

content also results in an improved electrical resistance.

With the above in view the invention consists in a method of treating articles of alkali-lime-silicate glass, including enamelled and glazed articles, which comprises subjecting said articles during their manufacture, while they are within the temperature range of 1000 to 450°C and in the absence of moisture, to the action of vapours of compounds which are volatile at the temperature of treatment and which are capable of modifying the composition of the said glass articles by forming glass components increasing the chemical resistance of the said glass article, said vapours being kept in motion so that they contact the entire surface of the said glass article, or in the case of a hollow glass article at least the entire outer or inner surface thereof, whereby in a superficial layer of the entire surface, or at least the entire inner or outer surface of the glass article, the composition of the glass is modified so as to form a surface layer which contains glass components increasing the resistance of the glass.

Specifically, the improvement of the surface is obtained according to this invention by subjecting the glass to the action of vapours of volatile substances, in particular metal compounds, which are capable of forming glass components which increase the chemical resistance of the glass, preferably in combination with gaseous substances which form compounds with the alkali in the surface layer of the glass.

It is important in order to obtain a durable and complete effect that the entire surface of the glass article be treated in a uniform manner (or at least the entire outer or inner surface, if the higher chemical resistance is required only on one side, e.g. in the case of bottles or tubes). It is essential that the

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entire glass article be coated by a sort of skin which contains resistance-improving glass components, and be also preferably completely free from alkali (or at least have a considerably lowered alkali content). There should be no areas in the surface which are untreated, since the attack may start in such areas. This is the more important as the alkali content near the surface is enriched during cooling of glass articles, a phenomenon which was suggested by investigations during the 1930's. Recent research has confirmed these findings; thus, the surface glass generally contains almost twice the amount of  $\text{Na}_2\text{O}$  (to the detriment of the  $\text{SiO}_2$  content) contained in the inner layers of the glass.

Thus, if the treatment is to have a durable effect, it must take place uniformly over the entire surface. This is possible only if the gases or vapours reacting with the glass are kept in continuous motion, e.g. by injection or by means of fans, by development of gases or the like, so that in fact the entire glass surface, or at least the inner or outer surface in the case of e.g. glass containers, is contacted with the gas. This circulation of the gases or vapours is essential, because the reactive gases and vapours involved are denser than air and would thus sink to the bottom, unless efficient circulation is maintained, whereby only the lower portion of the glass articles would be acted upon uniformly and reliably, and because e.g. in bottles the hot air in the article tends to prevent entrance of the reactive gases. Without the necessary methodical circulation of the gases or vapours at the temperature suitable for the reaction, the effect will be irregular. At most, either the inner or the outer surface only of the glass article will be influenced and in addition it will be influenced only incompletely and in the lower portion, in which case it may also happen that salts separated from the glass surface are fused into the glass at these portions.

Compounds which are used to incorporate resistance-increasing glass components include volatile compounds, such as halides and carbonyls, of aluminium, zinc, zirconium, chromium, molybdenum, tungsten, cobalt, nickel, boron, manganese, silicon, and so forth, the oxides of which elements when included in glass having a favourable influence on its characteristics. Thus, e.g. a treatment with aluminium chloride which results in the formation of feldspathic glass is found satisfactory.

In the method of this invention, very small amounts of these substances are sufficient to give the glass the desired surface resistance, while incorporation of oxides of the elements referred to by adding them to the glass melt would require vastly in-

creases quantities to achieve the desired result, and would moreover be very difficult or even impossible to carry out. In contrast, an incorporation by evaporation in accordance with this invention is simple and inexpensive in practice.

Examples of substances which are useful to de-alkalize the glass, include sulphur dioxide in combination with oxygen (air), sulphur trioxide and other acid gases, such as hydrogen chloride.

In a preferred embodiment of this invention, treatment is carried out with both de-alkalizing gases and volatile compounds forming resistance-increasing glass components. The de-alkalizing agent and volatile compounds may be applied simultaneously or they may be applied one after the other in either order.

A combination of the treatment with gaseous de-alkalizing agents and application of resistance-increasing substances, e.g. aluminium chloride, affords a valuable combination effect. It has been found that the adherence of the thin protective layer formed by application of the evaporated metal compound becomes much stronger if the glass surface is de-alkalized simultaneously or immediately after or before, whereby flaking of the protective layer, which could otherwise occur, is prevented.

Furthermore, if the alkali removed by the action of the acidic gases is replaced by other substances added simultaneously, the glass is rendered more resistant both chemically and mechanically, particularly if the surface of the glass article is simultaneously heated as explained in more detail below.

The combination of an acidic gas with a volatile metal compound, e.g. aluminium chloride, also gives a greater resistance not only against leaching of alkali, but also against leaching of silicic acid, because the de-alkalization residue,  $\text{CaO} \cdot 6\text{SiO}_2$ , is less stable than e.g. a feldspar glass,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

The action of aluminium chloride, whereby aluminium oxide is incorporated in a glass surface, has a double effect. Above all, the solubility of a feldspar glass is less than that of a "residual glass" having a high silicon and lime content and containing almost no alkali; at the same time, such a feldspar glass is chemically more resistant since a stable glass may be obtained from  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$  mixtures, while the above substantially de-alkalized residual glass is not stable at all as a glass necessarily requires alkali to be obtained in glass form. By replacing a water-susceptible alkali oxide glass by a water-resistant aluminium oxide-lime-silicate glass the glass state is maintained, which is not possible with lime-silica only.

Another advantage is that a thin surface layer of e.g. aluminium-containing glass gives improved dyeing characteristics which is of interest in particular in glass fibres. The adherence of organic dyes is improved by lake formation between the metal oxide, e.g.  $\text{Al}_2\text{O}_3$ , and the organic dyes. Soda glass on the other hand has a strong tendency for surface deterioration by hydrolysis, whereby the dye is loosened.

It has also been found that the treatment should be carried out at a temperature within the range of  $500^\circ$  to  $1000^\circ\text{C}$  and preferably at decreasing temperatures down to temperatures at which no subsequent diffusion of alkali oxide from the inner glass to the surface glass needs to be feared after the action of the gas has ceased. The temperature of treatment will lie within the range between a temperature where salt layers formed (e.g. alkali sulphate when  $\text{SO}_3$  is used) do not adhere to the glass but may be washed or wiped away, and the lowest temperature where alkali cannot migrate to the surface from the inner layers. In the case of alkali-lime-silicate glasses the range is between  $800^\circ$  to  $900^\circ\text{C}$  on one hand and  $400^\circ$  to  $450^\circ\text{C}$  on the other hand. Preferably, the de-alkalization should be carried out at decreasing temperatures within the range of  $600^\circ$  to  $500^\circ\text{C}$ . When sulphur dioxide (with air), hydrogen chloride or the like is allowed to act on the glass articles under these conditions, there is formed on the glass surface a very thin film which is free or substantially free from alkali. By treatment e.g. with sulphur dioxide in the presence of air under these conditions, the content of  $\text{Na}_2\text{O}$  in the surface layer may be reduced to a minimum. In the case of treatment with volatile resistance-increasing substances alone or in combination with de-alkalization, higher temperatures may be used. In certain cases it may be suitable or even necessary that the surface treatment takes place at substantially higher temperatures than  $600^\circ\text{C}$ , e.g. in the treatment of glass fibres, where the rate of production is so high that a sufficient surface improvement is achieved only if the substances act directly on the glass filaments already at the dies where the temperature is above  $1000^\circ\text{C}$ . On account of the high velocity there is no danger of burning in of alkali salts formed by the de-alkalization treatment despite the high temperature.

It has also been found that it is possible to deepen the thin transformed surface layer, if the glass when the temperature has dropped to a point not below about  $450^\circ\text{C}$  is heated only superficially from this temperature to about  $600^\circ$  to  $1000^\circ\text{C}$  and in connection with this brief superficial heating the reactive gases or vapours are allowed to act whereupon the conventional cooling is carried out during continued action of the

gases. If the inner portions of the glass are not heated, alkali cannot migrate to the surface and by this treatment a greater depth of the surface layer will be obtained.

This brief and only superficial heating of glass articles which are at medium temperatures may be carried out e.g. by subjecting the glass during cooling when the temperature has dropped to a point not below about  $450^\circ\text{C}$ , i.e. a temperature where the migration of alkali ions towards the surface has ceased, to the action of a gas heated to about  $600^\circ$  to  $1000^\circ\text{C}$ , e.g. by blowing.

It is preferable to apply the reactive substances in the last stage of moulding. For example, when drawing plate glass or glass tubes, the treatment may be carried out when the plate glass is being drawn out of the tank or the glass tube from the die. In the preparation of glass wool or glass fibres, the reactive substances may be applied when the glass wool is projected or the glass fibre leaves the die. When blowing bottles or bulbs the gas may be applied during the last stage of the blowing step, in which case it is suitably admixed to the blowing air. Other examples are manufacture of glass ampoules where the treatment may take place in connection with sealing, and manufacture of glass blocks where the treatment may be carried out in connection with the welding of the block halves. Sometimes, it may be more practical if the articles are subjected to the action of the reactive gases during cooling when the temperature suitable for the treatment is passed, thus e.g. in the manufacture of glass containers, glass insulators, glass tiles, glass mosaic or glazed articles, such as glazed ceramic bricks. The applications mentioned are only examples and the method may be adapted to any types of glass articles produced.

It is often suitable, in the stage of the manufacturing or cooling process where the temperature range suitable for the action of the reactive gases is passed, to introduce the glass articles into a closed casing or to surround the glass articles with such a casing, into which the gaseous substance is blown or the like or in which the substance is volatilized or kept in motion so that it contacts all parts of the surface of the glass articles. This casing is suitably used in the stage of the manufacturing process where the glass articles have already obtained substantially their final shape and the atmosphere has a temperature of  $450^\circ$  to  $600^\circ\text{C}$  or even higher provided that no deformation can take place. The gaseous substance may be drawn off and may be recycled. The surrounding casing not only ensures that the active gases will not be dissipated. For instance without the casing, in particular in the case of bottles and vessels with large mouths, the cold and therefore heavier air

would sink into the bottles, displace the gases and cool the glass surface so much as to prevent any remaining gases from reacting with the glass. Furthermore, the casing is 5 advantageous because it makes it easier to provide a uniform treatment of the entire surface by circulation.

As above mentioned, only small amounts of the reactive substances are required to 10 achieve the desired result. It is of importance, however, that the amounts of reactive substances supplied are carefully controlled, because too small amounts do not result in the desired improvement in resistance, while too 15 great a quantity may result in harmful crystallization effects on the glass surface. The amount per unit area shall correspond to that required to replace alkali superficially with aluminium oxide or the like plus an 20 excess necessary to compensate for losses in the treatment. The amount shall be kept as low as possible, since otherwise fused oxide deposits may have a disadvantageous effect. The exact amount in a given case is suit- 25 ably determined by preliminary trials.

The reactive substances may be supplied as solids, in solution or as vapours. In solid form they may be supplied e.g. as powders, tablets or the like which will be vapourized. 30 The preferred combination of volatile metal compounds and an acidic gas may be achieved in a simple manner by using a preparation made by fusing aluminium chloride and ammonium chloride together. While 35 each of these chlorides sublimates on heating, i.e. is vapourized without melting, in mixtures of the two salts melting takes place at temperatures between 150° and 300°C according to the composition of the mixture. 40 The essential advantage of this preparation is that it is less sensitive to moisture in the air than aluminium chloride alone. Only by using such combinations it is possible to achieve a correct dosage of aluminium 45 chloride and to prepare tablets.

The substances may be introduced in solution in suitable solvents which are supplied dropwise and evaporated. Examples of suitable solvents are carbon disulphide, 50 nitrobenzene and others. When using, e.g. a solution of aluminium chloride in carbon disulphide, the following reactions occur in the glass surface: Soda-lime-silicate glass + CS<sub>2</sub> + O<sub>2</sub> → de-alkalization residue + 55 Na<sub>2</sub>SO<sub>4</sub> + CO<sub>2</sub>. Soda-lime-silicate glass + AlCl<sub>3</sub> → lime-feldspar glass + NaCl. Investigations have shown that the former reaction may have a more or less marked depth effect, while the latter process mainly affects the 60 surface glass.

Furthermore, the reactive substances may be introduced in vapour form as a mixture or each gas separately. An automatic control of the dosage may be attained by utilizing 65 the variation of the vapour pressure of the

substances involved with the temperature.

In the case of some volatile substances, in particular AlCl<sub>3</sub>, it is of importance that this is anhydrous, since it has been found that a water-containing AlCl<sub>3</sub> has a weaker effect, 70 because the aluminium chloride is hydrolyzed and aluminium hydroxide does not react with glass in the same manner as aluminium chloride.

Even if the best effect of the surface treat- 75 ment is achieved by a combined action of the resistance-improving compounds and de-alkalizing agent, it is often sufficient if only said compounds are used, in particular if the stresses will not be excessive in the 80 practical use (i.e. if the glass articles are not heated or subjected to the action of acids or the like in the subsequent use). It will then be sufficient e.g. with a feldspathization by the action of aluminium chloride. 85

By the de-alkalization treatment, alkali sulphate, alkali chloride or the like will be formed on the glass surface. In most cases, these substances may be easily removed. In cases, e.g. glass wool, where this is not easily 90 achieved, the salt formed may without disadvantage be allowed to remain on the glass surface.

The treatment according to this invention may be applied not only to articles of glass 95 in the usual sense, but also to articles which are enamelled or glazed, since enamels and glazes are equivalent to glass in their composition.

#### WHAT I CLAIM IS:—

1. A method of treating articles of alkali-lime-silicate glass, including enamelled and glazed articles, which comprises subjecting said articles during their manufacture, while they are within the temperature range of 1000 to 450°C and in the absence of moisture, to the action of vapours of com- 105 pounds which are volatile at the temperature of treatment and which are capable of modifying the composition of the said glass article by forming glass components increas- 110 ing the chemical resistance of the said glass article, said vapours being kept in motion so that they contact the entire surface of the said glass article, or in the case of a hollow glass article at least the entire outer or inner surface thereof, whereby in a super- 115 ficial layer of the entire surface, or at least the entire inner or outer surface of the glass article, the composition of the glass is modified so as to form a surface layer which contains glass components increasing the resistance of the glass. 120

2. A method as claimed in claim 1, in which said articles are also treated with 125 gaseous substances which may form compounds with alkali in the surface layer, in particular acidic gases, such as sulphur dioxide together with oxygen, such as atmospheric oxygen, or sulphur trioxide or 130

hydrogen chloride.

3. A method as claimed in claim 1 or 2, in which said volatile compounds are compounds, such as halides or carbonyls, of  
5 aluminium, zinc, zirconium, chromium, molybdenum, tungsten, cobalt, nickel, boron, manganese or silicon.

4. A method as claimed in any preceding claim, in which said treatment is carried out  
10 at a decreasing temperature until it has become so low that diffusion of alkali in the glass has practically ceased.

5. A method as claimed in any of claims 1 to 3, in which the treatment is carried out  
15 when the glass has been cooled to not below about 450°C by reheating the glass only superficially to about 600°C to 1000°C while simultaneously subjecting the surface

to reactive gases or vapours, whereupon final cooling takes place.

6. A method as claimed in any of claims 1 to 5, in which the glass articles, when they are in that stage of the manufacturing or cooling process, wherein the temperature range suitable for the action of the reactive  
25 gases is passed, are introduced into a closed casing into which the gaseous substances are introduced.

7. A method as claimed in claim 3, in which the volatile compounds are used in  
30 an anhydrous state.

8. A method of treating articles of alkali-lime-silicate glass, substantially as hereinbefore described.

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